

⑪ ⑧ No. 1043322

⑯ ISSUED 781128

⑮ CLASS 253-128
C.R. CL.

⑯ INT. CL. ² C10M 1/14, 1/18

⑯ ⑧ CANADIAN PATENT ⑯

⑯ MULTIGRADE LUBRICANTS CONTAINING NON-AROMATIC
MONO-OLEFIN POLYMERS

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Granted to The Lubrizol Corporation,
U.S.A.

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⑯ APPLICATION No. 209,981

⑯ FILED 740923

⑯ PRIORITY DATE U.S.A. (402,231) 731001

NO. OF CLAIMS 27 - No drawing

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FIELD OF THE INVENTION

5 This invention concerns lubricating oil compositions which are especially adapted for use in mechanical systems where gears are subjected to great stresses and extremely high pressures such as those found in automotive rear axles and tractor transmissions. In particular, the invention concerns a gear lubricant comprising in combination a base oil, at least one polymer of specified structure and molecular weight, and at least one extreme pressure or load-carrying agent.

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BACKGROUND OF THE INVENTION

15 The problems associated with the lubrication of automotive rear axle and transmission gears are well known to those of skill in the art. Such gears are usually hypoid in nature and for reasons inherent in their design develop great pressures between the contacting metal surfaces of the gear. These pressures literally squeeze out ordinary mineral oil lubricants from between the gears and result in metal-to-metal contact between the parts of the gear under extreme high pressures. Such metal-to-metal contact soon leads to deformation and destruction of the gear surfaces.

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25 To alleviate these and other problems it has become a common practice to add to gear oils certain chemical substances which are generally called additives. Among such additives are extreme pressure agents which are widely believed to react with the metal surfaces of the gear under the elevated temperatures and high pressures generally encountered during operation of the gear to form thin films. These newly formed layers act as separants

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1043322

and lubricants for the gear surfaces and thus prevent or reduce destructive metal-to-metal contact.

5 Recently a demand has arisen for lubricants which will function satisfactorily as gear lubricants under a wide range of temperature conditions. Such compositions are characterized by a relatively small change in their viscosity with changing temperature and they are commonly graded according to SAE standards according to their viscosities at low (e.g., 0°F.) and high temperatures (e.g., 210°F.).

10 Because of this grading, such gear oils are often said to be "multigraded." In terms of widely accepted concepts such multigraded gear lubricants can also be said to have high viscosity indices. Multigraded gear lubricants thus have the desirable property of being able to function immediately, though cold, upon being put into service and continue to function satisfactorily as they become heated during operation.

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20 In addition to being multigraded, it is desirable that lubricant compositions especially adapted for use as gear lubricants exhibit shear stability. This means that they will not degrade or lose their viscosity as a result of the shearing forces encountered during their use.

25 Compositions exhibiting desirable shear stability will be found to generally have a viscosity within 85 to 95% of their original viscosity after many hours (say 1000) of service. It has been recognized that many ordinary viscosity index improvers commonly added to crankcase lubricating oils, such as high molecular weight polyisobutylene and polyacrylates, do not possess the desired shear stability for use in improving the viscosity properties of gear lubricants.

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1043322

5 It has now been found that, multigrade lubricants exhibiting exceptional shear stabilities can be made by combining in certain proportions base oils, polymers of specified structure and molecular weight and extreme pressure agents.

10 SUMMARY OF THE INVENTION

15 The lubricants of the present invention comprise (A) about 95 to about 30, preferably about 90 to about 50, weight percent of a base oil (B) at least one extreme pressure agent in an amount sufficient to improve the extreme pressure properties thereof, and (C) about 5 to about 70 weight percent of at least one oil-soluble polymer, said polymer being a homopolymer of a non-aromatic monoolefin having at least three carbon atoms and having a number average molecular weight (M_n) of about 750 to about 10,000, and present in an amount sufficient to make the lubricant SAE multigraded between SAE 75W and SAE 250.

20 DESCRIPTION OF SPECIFIC EMBODIMENTS

25 The base oils of the present invention, that is, component (A), have viscosities of about 40 to about 2000 SUS (Saybolt Universal Seconds) at 100°F. Preferably they have viscosities of about 75 to about 500 SUS at 100°F., and most preferably of about 100 to about 300 SUS at 100°F. These base oils may be natural oils, synthetic oils, or they can be combinations of two or more of these types of oils; e.g., combinations of different natural oils, combinations of different synthetic oils, or combinations of one or more natural oils with one or more synthetic oils. Selection of materials suitable as base oils is within the skill of the art using the parameters herein set forth.

30 When the base oil is a mixture of natural and

1043322

synthetic oils, the mixture contains about 5 to about 95 weight percent of at least one synthetic oil. Preferably such mixtures contain 40 to about 90% natural oil and 60 to about 10% synthetic oil. Of course, both the natural oils and synthetic oils can themselves be mixtures of various types of natural oils or synthetic oils.

5 When the base oil consists of natural oils, they are often derived from petroleum, although oils derived from other natural sources such as shale, coal, animals and plants can also be used. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those of skill in the art. All that is required of oils useful in this invention is that they have viscosities falling within the above-noted ranges which enable the final composition to have the below-recited SAE multigrade properties and that they be generally compatible with the other components of the gear lubricant and the materials used in construction of the gear assemblies in which they function.

20 25 As is noted above, the base oil can consist essentially of or comprise a portion of one or more synthetic oils. Among the suitable synthetic oils are homo- and interpolymers of C_{2-12} olefins, carboxylic acid esters of both monoalcohols and polyols, polyethers, silicones, polyglycols, silicates, alkylated aromatics, carbonates, thiocarbonates, orthoformates, phosphates and phosphites, borates and halogenated hydrocarbons. Representative of such oils are homo-

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1043322

and interpolymers of C_{2-12} mono-hydrocarbyl olefins, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di(2-ethylhexyl)benzenes, wax alkylated naphthalenes, etc.); polyphenyls (e.g. biphenyls, terphenyls, etc.); and the like.

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Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of useful synthetic oils. These are exemplified by the oils prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol. Among such glycols are the polyalkylene glycols sold by the Union Carbide Corporation of New York under UCON LB-135*, UCON LB-385*, and UCON LB-1145*.

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Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, maleic acid, azellic acid, suberic acid, sebatic acid, fumaric acid, adipic acid, linoleic acid dimer, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisododecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the

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1043322

complex ester formed by reacting one mole of sebamic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like. Among the halogenated hydrocarbons useful as base oils are chlorinated phenyl and biphenyls, low molecular weight chlorotrifluoro ethylene polymers, polytetrafluoroethylenes of appropriate molecular weights, and the like.

10 Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, etc.

20 Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-1-tetraethyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexyl-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)siloxanes, poly(methylphenyl)-siloxanes, etc.). Among these are the oils sold by the Dow Chemical Co. of Michigan, under DC-200*, DC-500*, and DC-700*. Other synthetic lubricating oils include liquid esters of phosphorus containing acids (e.g. tricresyl phosphate, tricetyl phosphate, triphenyl phosphite, diethyl ester of decane phosphonic acid, etc.).

Organic carbonates and thiocarbonates such as those formed from the well known Oxo alcohols as well as orthoformates, mercaptals, thiol or thioformates and the like

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1043322

can also be used as synthetic oils in this invention, if in the form they are used (e.g., as blends) they exhibit viscosities within the aforesaid limits.

5 The fact that the base oils of this invention may consist of natural, synthetic, or natural-synthetic blended oils does not mean that these three types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain inventive compositions for the specific properties they possess such as non-flammability or lack of corrosivity towards specific metals (e.g., silver or cadmium) which are used in certain specialized gear assemblies. In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the three types of base oils discussed above are all useful in the compositions of the present invention, they are not necessarily functional equivalents of each other in every instance.

20 It is preferable that, if the lubricants of the present invention consists essentially of only one synthetic base oil and only one polymer, i.e., component (C), the base oil should not be derived from the same olefin as the polymer. Thus, for example, if the polymer is a polybutene, it is preferable that the base oil not consist essentially of only polybutene. If, however, the base oil is a polypropene or a mixture of polybutene and mineral oil, then the polymer can be a polybutene and so forth.

25 30 As is clear from the above discussion, in certain embodiments of this invention the synthetic oil is not solely hydrocarbyl in nature, but can contain atoms of oxygen, sulfur, silicon, halogen, as well as those of carbon

1043322

and hydrogen, etc.; of course, in other embodiments the synthetic oil will be solely hydrocarbyl in nature. This is also true of the natural oils used in this invention.

5 In many embodiments it is preferable that the synthetic oil have a number average molecular weight below about 800. Naturally, such oils must also conform to the viscosity limitations set forth above.

10 A second component of the gear oils of this invention, that is, component (C), is at least one oil-soluble polymer selected from the group consisting of homopolymers of non-aromatic monoolefins having at least three carbon atoms.

15 The characterization of these polymers as oil-soluble does not necessarily mean they are soluble in all base oils in all proportions; it means they are soluble in the base oils with which they are formulated to a degree sufficient to allow the lubricant composition to be multi-graded between SAE 75W and SAE 250. These polymers have the common property of having number average molecular weights within the range of about 750 to about 10,000; preferably their molecular weights lie between about 900 and about 5,000.

20 The above-mentioned homopolymers can be prepared from non-aromatic monoolefins having at least three carbon atoms and preferably no more than twenty carbon atoms by a number of polymerization techniques well known to those of skill in the art. It should be noted that "homopolymer" as used herein, describes polymers made from monoolefins having the same number of carbon atoms. Thus, polymers made from a mixture of butene-1 and isobutylene are, in the terms of this specification and the appended claims, homo-

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1043322

polymers of butylene. When they contain predominantly units derived from a single isomer, they may be referred to as polymers of that isomer; but, such terminology does not exclude the possibility of the presence of a minor amount of units derived from other isomers. Thus, a "polyisobutylene polymer" might contain units, 80% of which are derived from isobutylene, 15% from 1-butene and 5% from 2-butene.

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Particularly preferred are homopolymers made from C_3 to C_{20} monoolefins such as propene, 2-butene, isobutene, hexene-1, decene-3, tetradecene-4, etc. More preferable are homopolymers derived from C_4 to C_8 1-olefins such as butane, isobutane, pentene-1, heptene-1, etc. The most preferred homopolymers are those of propene and the various butenes.

Techniques such as Ziegler, cationic, free-radical, anionic, emulsion polymerization and so forth can be used in appropriate circumstances to prepare these polymers. A particularly convenient technique for polymerizing such olefins for use in this invention is through the use of a Lewis acid catalyst such as aluminum chloride, boron trifluoride, titanium tetrafluoride and the like. These polymerizations are well known in the art and need not be described further at this point.

Among the polymers that are useful in the compositions of the present invention are the following: a polyisobutene of M_n 1300, a poly(1-octene) of M_n 4300, a poly(3-heptene) of M_n 900, a poly(1-eicosene) of M_n of 9500, a poly(1-nonen) of M_n 3700, a poly(2-methyl-1-pentene) of M_n 1700, a poly(5-ethyl-1-hexene) of M_n of 2200, and a poly(8-methyl-1-tetradecene) of M_n 1900.

1043322

In general, it is preferred that the polymers of the present invention, i.e., component (C), for reasons of oxidative stability, contain no more than five percent unsaturation on the basis of the total number of carbon-to-carbon covalent linkages present within an average molecule. Such unsaturation can be measured by a number of means well known to those of skill in the art, such as infrared, NMR, etc. Most preferably these polymers contain no discernable unsaturation.

A particularly preferred polymer meeting all the above requirements is polyisobutene, although other polymers such as polypropylene may also prove equally useful and desirable.

The third component, i.e., component (B), of the lubricant compositions of this invention, is an oil-soluble extreme pressure agent, or a combination of two or more such agents. Substances which function as extreme pressure agents in lubricating oils are of an extremely diverse nature as is well known to those of skill in the art. See, for example, the particularly useful discussions in the books "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lexius-Hiles Co. Publishers, Cleveland, Ohio, 1967), pages 9 et seq.; "Gear and Transmission Lubricants", by C.T. Bonor (Reinhold Publishing Corp., New York, 1964), pages 85-100; and "Lubricant Additives" by M.W. Ranney (Noyes Data Corporation, New Jersey, 1973), pages 146-221. These publications discuss how to make and/or use extreme pressure agents as well as discuss the state of the art with regard to extreme pressure agents.

Among the types of compounds known by those

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1043322

skilled in the art to be useful as extreme pressure agents in the lubricating compositions and, therefore, useful as component (D) of this invention, are organo-boron, organo-sulfur, organo-halogen, organo-halo-sulfur, organo-phosphorus, organo-halo-phosphorus, and organo-thiophosphorus compounds as well as esters, amides, and salts of phosphorus and carboxylic acids and oil-soluble molybdenum-containing complexes such as those disclosed in U.S. patent 3,541,014. Each of these types of compounds can be exemplified by the following:

(1) Borate esters of C_{1-6} alkanols and adducts prepared by reaction of succinimides of polyalkylene amines and boric acid. Specific examples include trioctyl borate and the adduct formed by reaction of boric acid with a polyisobutetyl succinimide of tetraethylene pentamine.

(2) Sulfurized olefins, sulfurized fatty acid esters of both natural (e.g., sperm oil) and synthetic origins, tritilones, thienyl derivatives, sulfurized terpenes, sulfurized oligomers of C_{2-6} monoolefins, xanthates of alkancis and other organo-hydroxy compounds such as phenols, thiocarbamates made from alkyl amines and other organo amines, etc.; sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent RE 27,331. Specific examples include sulfurized polyisobutene of Mn 1100, sulfurized triisobutene, dicyclohexyl disulfide, diphenyl and dibenzyl disulfide, etc.

(3) Chlorinated waxes of both the paraffinic and microcrystalline type, polyhaloaromatics such as di- and trichlorobenzene, trifluoromethyl naphthalenes, perchloro-benzene, pentachlorophenol, dichloro diphenyl trichloro-

ethane, etc.

(4) Chlorosulfurized olefins and olefinic waxes, sulfurized chlorophenyl methyl chlorides, chloroxanthates, etc.; specific examples include chlorodibenzyl disulfide, chlorosulfurized polyisobutene of Mn 600, chlorosulfurized pinene and lard oil, etc.

(5) Trialkyl and triaryl phosphites, phosphonates and phosphates, dihydrocarbyl phosphites, etc.; such as tricresyl phosphate, tributyl phosphite, tris(2-chloroethyl)phosphate and phosphite, dibutyl trichloromethyl phosphonates, di(n-butyl) phosphite, tolyl phosphinic acid dipropyl ester, etc.

10 (6) Metal dithio dihydrocarbyl phosphates, particularly those of lead and zinc, phosphorus pentasulfideolefin reaction products, esters of dithiophosphorus acids, esters and salts of thio and dithiophosphates, etc. Specific examples include lead, zinc and sodium dioctyl dithiophosphates, lead and zinc dibenzyl dithiophosphates, etc.

(7) Reaction products of olefin oxides (e.g., ethylene and propylene oxide) and phosphorus halides oxyhalides or thiohalides, reaction products of phosphites and chloral or bromal, chloro- and bromo-alkyl phosphites and phosphates and amine salts thereof, etc.

(8) Phosphate salts of amines, ammonia and metals, analogous phosphonic acid derivatives, neutral phosphites, phosphonites, phosphates and phosphonates and their thioanalogs, etc. Specific examples include the dihexyl ammonium salt of trichloromethane phosphonic acid, the diethyl hexyl ammonium salt of dioctyl dithiophosphate, etc.

(9) Fatty acids, dimerized and trimerized unsaturated

1043322

natural acids (e.g., linoleic) and esters, amine, ammonia, and metal (particularly lead) salts thereof, and amides and imidazoline salt and condensation products thereof, oxazolines, and esters of fatty acids, such as ammonium di-
5 (linoleic) acid, lard oil, oleic acid, animal glycerides, lead stearate, etc.

Many of these extreme pressure agents and further specific examples are described in detail in the aforementioned books, "Lubricant Additives" and "Gear and
10 Transmission Lubricants".

Particular classes of extreme pressure agents useful in this invention are the sulfurized hydrocarbons and organo-thiophosphonyl salts, and mixtures of such compounds. The preparation of such compounds is well known
15 in the art. See, for example, the disclosures of U.S. Patents 3,231,558 and 3,197,405, and the above-noted books. In brief, the organo-sulfur compounds are made by reacting an organic material such as isobutylene with a halosulfurizing agent such as sulfur monochloride and subsequently treating the
20 intermediate formed with a sulfurizing agent such as sodium sulfide or polysulfide to produce the desired organo-sulfur extreme pressure agent. The organo-thiophosphorus compounds are conveniently made by reacting a phosphorous sulfide
25 (e.g., P_4S_10) with a mercaptan or alcohol.

At least one of the afore-described extreme pressure agents is present in the compositions of this invention in an amount sufficient to improve the extreme pressure properties of the composition. In general, this amount will be about 0.25 to about 20 weight percent of the total composition. More preferably, it ranges from about
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1043322

0.5 to about 10 weight percent of the total composition.

Often it is desirable to use combinations of two or more of the above-described extreme pressure agents. Such combinations can include mixtures of two or more compounds selected from a single class, or compounds selected from two or more classes of extreme pressure agents. Whatever the particular combination is, however, the total amount of extreme pressure agent will fall within the above-recited ranges.

10 Lubricating oils for gears can be classified according to a scheme introduced by the American Society of Automotive Engineers (SAE). According to this so-called SAE classification such lubricating oils are classified into two groups on the basis of their minimum viscosities at 210°F., (98°C). These groups are the winter grades and the normal grades. Each of the two groups is divided into a number of classes. The classes of the winter grades are indicated with the letter W preceded by a number, e.g., a 75W, 80W or 85W oil. The winter grades have a specified minimum viscosity at 210°F. The classes of the normal grades are indicated by a number only, viz. a 90, 140 or 250 oil. The normal grades must have a viscosity at 210°F. within a specified range. Generally, oils complying to a certain winter grade do not comply with the viscosity requirement for any normal grade as well, and, conversely, oils complying to a certain normal grade do not comply with the viscosity requirement for a winter grade. Lubricating oils that fall within one SAE class only (viz. either comply with a normal or a winter grade) are designated as single-grade lubricating oils. Examples of widely used single-grade lubricating oils are SAE 75W and SAE 90 oils.

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On the other hand, lubricating oils which do in fact comply with the specification of both a winter grade and a normal grade are designated as multigrade lubricating oils.

It is a particular feature of the compositions of this invention that they may be multigraded according to SAE standards within the multigrade range lying between SAE 75W and SAE 250. This means that the compositions have viscosities which allow them to be characterized as multigrade; that is, they may be, for example, SAE 75W/85W, SAE 90/250, SAE 85W/140 and so forth. The viscosity properties required to be exhibited by compositions meeting such standards are summarized in the following table:

----- TABLE I -----

		SAE 75W	SAE 80W	SAE 85W	SAE 90	SAE 140	SAE 250
15	Vis. @ 210°F (99°C) (a)						
	Min. (cSt) (b)	4.2	7.0	11.0	14.0	25.0	43.0
	Max. (cSt)	no req.	no req.	no req.	25.0	43.0	no req.
20	Min. (SUS) (c)	40.0	46.0	63.0	74.0	120.0	200.0
	Max. (SUS)	no req.	no req.	no req.	120.0	200.0	no req.

(a) Viscosities determined by ASTM D-445 procedure as set forth by the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103, U.S.A.

(b) Centistokes

25 (c) Saybolt Universal Seconds

Thus the lower SAE value is the minimum viscosity the oil can have (and still meet the standard), while the upper value is the maximum viscosity the oil can have. For example, an oil multigraded as SAE 75W/90 has (as the data in Table I shows) a minimum viscosity of 4.2 cSt (or 40 SUS) at 210°F. and a maximum viscosity of 25 cSt (or 120 SUS) at 210°F., while an oil multigraded as SAE 90/140 has a minimum viscosity of 14.0 cSt (or 74.0 SUS) and a maximum

1043322

viscosity of 47.0 cSt (or 200 SUS), both measured at 210°F.

It is these viscosity properties which make the compositions of this invention especially useful since they can function satisfactorily over a wide range of temperatures. Thus, the compositions can function to lubricate a gear at extremely cold temperatures during start-up or while flying at high altitude and still maintain satisfactory lubricating properties well after operation of the gear has resulted in a substantial increase in temperature or the gear-containing device has returned to a warm environment.

Many of the preferred embodiments of this invention are also characterized by properties which permit them to conform with the requirements of MIL-L-2105B specifications promulgated by the U.S. Government for gear lubricants. They thus possess adequate properties with respect to foaming, thermal and oxidative stability, water separation, compatibility and copper corrosion.

In addition to the three essential components discussed above, the compositions of this invention can also include other conventional lubricant additives which confer a variety of beneficial properties upon the composition. Such additives as antiwear agents and additives to improve the load-carrying properties of lubricants such as tri-hydrocarbyl phosphates or metal, particularly zinc hydrocarbyl dithiophosphates; antioxidants such as hindered alkyl phenols (e.g., 2,6-Di-t-butyl-4-methyl phenol); rust inhibitors such as alkylated succinic acids and anhydrides or calcium, barium or sodium sulfonates; ashless detergent/dispersants such as those noted below; ash-forming detergent/dispersants such as metal phenates and sulfonates;

1043322

anti-foaming agents, such as silicones, anti-friction agents, such as stearyl alcohol or stearyl cyanide; dyes, metal deactivators and so forth may be included in appropriate amounts, in the composition of this invention.

5 Among the ashless detergent/dispersants which can be used to advantage in the oil compositions of this invention are those which are formed by reaction of a mono-alcohol or polyol with a high molecular weight mono- or polycarboxylic acid acylating agent containing at least
10 thirty carbon atoms in the acyl moiety. Such ester compositions are well known to those of skill in the art. See, for example, French Patent Specification 1,396,645, British Patent Specifications 981,850; 1,055,337; and 1,306,529 as well as U.S. Patents 3,255,108; 3,311,588; 3,311,776; 15 3,346,345; 3,381,022; 3,522,179; 3,542,680; 3,576,743; 3,579,450; 3,632,510; and 3,639,242. Each of the foregoing U.S. and foreign patent publications describe how to make and use such compositions.

20 Another type of particularly useful ashless dispersant is formed by the reaction of a mono- or polycarboxylic acid acylating agent with polyamines. Other related useful dispersants can be prepared by post-treating such dispersants with alkoxides, cyanides, etc. See, for example, U.S. Patents, RE 26,433; 3,172,892; 3,216,936; 25 3,219,666; 3,256,185; 3,272,746; 3,278,550; 3,306,493; 3,341,542; 3,366,569; 3,373,111; 3,374,174; 3,502,671; 3,541,012. Other useful ashless dispersants are formed by the reaction of a halogenated polymer with a polyalkylene polyamine. Such dispersants are described in U.S. Patents 30 3,573,010; 3,574,576; 3,498,757; 3,565,804; and 3,565,492.

1043322

Still other ashless dispersants are formed by reaction of an alkylated phenol, a lower aldehyde and an amine or polyamine via the well-known Mannich reaction. The preparation of such materials in lubricants are disclosed in U.S. Patents 3,036,003; 3,368,972; 3,413,347, 3,448,047; 3,539,633; and 3,649,229.

A particularly useful type of additive often included in compositions of this invention is one or more pour point depressants. The use of such pour point depressants in oil-base compositions to improve the low temperature properties of the compositions is well known to the art. See, for example, the aforementioned book "Lubricant Additives" by Smalheer and Smith, page 8, and "Gear and Transmission Lubricants", p. 102, and "Lubricant Additives" by Ranney. Among the types of compounds which function satisfactorily as pour point depressants in the composition of the present invention are polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, and vinyl carboxylate polymers. A particularly useful class of pour point depressants are terpolymers made by polymerizing a dialkyl fumarate, vinyl ester of a fatty acid and a vinyl alkyl ether. Techniques for preparing such polymers and their uses are disclosed in U.S. patent 3,250,715. Generally, when they are present, in the compositions of this invention, the pour point depressants are present in the amount of 0.01 to about 5 weight percent of the total composition.

1043322

Examples

It is believed that the nature of the invention may be more accurately appreciated from a study of the following examples which are given mainly for illustrative purposes and are in no way intended to limit the scope of the claimed invention.

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A number of compositions embodying the present invention are prepared by blending together the components outlined in Table II in the indicated proportions which are all percentages by weight. The viscosity properties of these compositions are also summarized in Table II. It should be noted that where the percentages of components does not add up to 100, the balance of the composition consists of a pour point depressing terpolymer of a C₁₂-C₁₄ fumarate diester, ethyl vinyl ether and vinyl acetate.

The extreme pressure agents used in preparing these blends of Examples 1-10 are all commercially available mixtures comprising organo-thiophosphonyl salts and sulfurized hydrocarbons sold by The Lubrizol Corporation of Cleveland, Ohio, under Anglamol 93*, Anglamol 98A* and Anglamol 99*.

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As can be seen from an examination of the data in Table II, each of the blends of Examples 1-10 is multigraded according to SAE standards between SAE 75W and SAE 250. These blends also satisfactorily lubricate automotive differential gears and exhibit outstanding shear resistant properties over prolonged use.

Lubricating oil concentrates can also be used conveniently to prepare such compositions, and are within the scope of the present invention. For example, a similar composition to that of Example 6 can be prepared by first

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1043322

5 forming a concentrate of polymer, extreme pressure agent and pour point depressant in the relative amounts of 62 parts, 16 parts and 1 part in 21 parts of solvent neutral diluent oil (all parts by weight). Such a concentrate is then blended with an equal part of an appropriate synthetic alkylated aromatic oil to form a composition closely resembling that of Example 6.

10 These concentrates comprise (B) at least one of the afore-described extreme pressure agents and (C) homo-
15 polymers, the amounts of (B) and (C) incorporated in said concentrate being such that when about 75 to about 25 parts by weight of the concentrate is blended with about 25 to 75 parts by weight of at least one natural, synthetic or synthetic-natural oil mixture having a viscosity of about 20 to about 2000 SUS at 100°F., the resulting blend is a lubricating oil composition multigraded according to SAE standards within the multigrade range of SAE 75W to SAE 250.

20 For example, these concentrates comprise about 15 to 70 percent of an oil (which can be natural, synthetic or a mixture of the two), about 85 to 30 percent of the afore-described polymer and about 5 to about 30 percent of the afore-described extreme pressure agents. Optionally such concentrates can also contain about 0.5 to about 5 percent of a pour point depressant.

1043322

TABLE II

Ex.	Type	Base Oil	Amount, % ¹	Polymer		Extreme Pressure Agent		Viscosity Grade 80W/90
				Type ² PBI	Mn 1300	Amount, % ¹	Type Anglamol 99 *	
1	150 Solvent Neutral	46.2						
	650 Solvent Neutral	30.8						
2	150 Bright Stock	34.5	PBI	1300	23	Anglamol 99 *	6.5	80W/140
	100 Naphthenic Neutral							
3	200 Solvent Neutral	41.5	PBI	900	50	Anglamol 99 *	6.5	85W/250
4	200 Solvent Neutral	59.5	PBI	900	32	Anglamol 98A *	8.0	80W/90
5	200 Solvent Neutral	50.5	PBI	900	40	Anglamol 99 *	8.5	85W/140
6	Synthetic Alkylated Aromatics (Mn = 190)	50	PBI	900	31	Anglamol 98A *	8.0	75W/90
	100 Solvent Neutral	10.5						
7	100 Solvent Neutral Synthetic Alkylated Aromatics (Mn = 350)	32.25	PBI	1300	27	Anglamol 99 *	6.5	75W/90
8	Pentaerythritol Ester ₁	59.5	PBI	900	32	Anglamol 98A *	8.0	80W/90
9	150 Solvent Neutral	45	PBI	1300	45	Anglamol 93 *	10.0	85W/90
10	100 Naphthenic Neutral	45	PP	1500	37	Anglamol 98A *	8.0	80W/140
	300 Solvent Neutral	20						

• TRADE MARK

¹All amounts in weight percentages
²PBI = Polyisobutylene; PP = polypropylene

1043322

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a multigraded gear oil composition comprising (A) about 95 to about 30 weight percent of a base oil having a viscosity of about 40 to about 2000 SUS at 100°F. and (B) at least one extreme pressure agent in an amount sufficient to impart extreme pressure properties thereto, the improvement in said composition comprising incorporating therein (C) about 5 to about 70 weight percent of at least one oil-soluble homopolymer of a non-aromatic monoolefin having at least 3 carbon atoms, said polymer having a number average molecular weight of about 750 to about 10,000 and present in an amount so as to allow the lubricating oil composition to be multigraded according to SAE standards in the multigrade range between SAE 75W and SAE 250, and said base oil being selected from the group consisting of natural oil, synthetic oils and mixtures of about 5 to about 95 weight percent of at least one natural oil and about 95 to about 5 weight percent of at least one synthetic oil.
2. A composition as claimed in claim 1 wherein the base oil has a viscosity of about 75 to about 500 SUS at 100°F.
3. A composition as claimed in claim 1 wherein the base oil has a viscosity of about 100 to about 300 SUS at 100°F.
4. A composition as claimed in claim 1 wherein the amount of extreme pressure agent is from about 0.25 to about 20 weight percent of the total composition.
5. A composition as claimed in claim 4 wherein the extreme pressure agent is selected from the group consisting of organo-

1043322

boron-, organo-sulfur-, organo-halo-, organo-halo-sulfur-, organo-phosphorus-, and organo-thiophosphorus-compounds and esters, amides and salts of phosphorus and carboxylic acids.

6. A composition as claimed in claim 5 wherein the extreme pressure agent is a mixture of organo-thiophosphonyl salts and sulfurized hydrocarbons.

7. A composition comprising the composition of claim 1 and about 0.01 to about 5 weight percent of at least one pour point depressant.

8. A composition as claimed in claim 7 wherein the pour point depressant is selected from the group consisting of polymethacrylates, polyacrylates, condensation products of haloparaffin waxes and aromatic compounds, vinyl carboxylates and terpolymers of fumarate alkyl esters, vinyl alkyl ethers and vinyl carboxylates.

9. A composition as claimed in claim 8 wherein the pour point depressant is a terpolymer of a dialkyl fumarate, alkyl vinyl ether, and vinyl carboxylate.

10. A composition as claimed in claim 1 wherein the homopolymer is derived from a C₃-C₂₀ olefin.

11. A composition as claimed in claim 10 wherein the polymer has a number average molecular weight of about 900 to about 5000.

12. A composition as claimed in claim 11 wherein the homopolymer is derived from a C₄-C₈ 1-olefin.

13. A composition as claimed in claim 12 wherein the homopolymer is derived from propene or a butene.

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14. A composition as claimed in claim 1 wherein the polymer has a number average molecular weight of about 900 to about 5000.

15. In a lubricating oil composition comprising (A) about 90 to about 50 weight percent of a base oil consisting essentially of natural oil having a viscosity of about 75 to about 500 SUS at 100°F., and (B) about 0.25 to about 20 weight percent of at least one extreme pressure agent selected from the group consisting of organo-thiophosphonyl salts, sulfurized hydrocarbons and mixtures thereof, the improvement which comprises incorporating therein (C) about 10 to about 50 weight percent of at least one oil-soluble homopolymer of a non-aromatic monoolefin having between three and twenty carbon atoms, said polymer having a number average molecular weight of about 750 to about 10,000, and present in an amount so as to allow the lubricating oil composition to be multi-graded according to SAE standards in the multigrade range between SAE 75W and SAE 250.

16. A composition as claimed in claim 15 wherein the homopolymer is polyisobutene having a number average molecular weight of about 900 to about 5000.

17. In a lubricating oil composition comprising (A) about 90 to about 50 weight percent of a base oil having a viscosity of about 75 to about 500 SUS at 100°F., said base oil comprising a mixture of about 5 to about 95 weight percent of at least one natural oil and about 95 to about 5 weight percent of at least one synthetic oil, and (B) about 0.25 to about 20 weight percent of at least one extreme pressure agent selected from the group consisting of organo-thiophosphonyl salts, sulfurized hydrocarbons and mixtures thereof, the improvement which comprises incorporating therein

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1043322

(C) about 10 to about 50 weight percent of at least one oil-soluble homopolymer of a non-aromatic monoolefin having between three and twenty carbon atoms, said polymer having a number average molecular weight of about 750 to about 10,000, and present in an amount so as to allow the lubricating oil composition to be multi-graded according to SAE standards in the multigrade range between SAE 75W and SAE 250.

18. A composition as claimed in claim 17 wherein the homopolymer is polyisobutene having a number average molecular weight of about 900 to about 5000.

19. A composition as claimed in claim 1 wherein the synthetic oil is not derived from the same olefins as the polymer.

20. A composition as claimed in claim 1 wherein the synthetic oil is not solely hydrocarbyl in composition.

21. A composition as claimed in claim 1 wherein the synthetic oil is selected from the group consisting of homopolymers and interpolymers of C₂-C₁₂ olefins, carboxylic acid esters, carbonates, thiocarbonates, orthofumarates, phosphates, phosphites, alkylated aromatics, silicones, polyglycols, polyethers, silicates, and halogenated hydrocarbons.

22. A composition as claimed in claim 1 wherein the base oil comprises about 40 to about 90 weight percent of at least one natural oil and about 60 to about 10 weight percent of at least one synthetic oil.

23. The composition as claimed in claim 1 wherein the synthetic oil has a number average molecular weight below about 800.

1043322

24. In a lubricating oil composition comprising (A) about 90 to about 30 weight percent of a base oil consisting essentially of synthetic oil having a viscosity of about 75 to about 500 SUS at 100°F., and (B) about 0.25 to about 20 weight percent of at least one extreme pressure agent selected from the group consisting of organo-thiophosphonyl salts, sulfurized hydrocarbons and mixtures thereof, the improvement which comprises incorporating therein (C) about 10 to about 50 weight percent of at least one oil-soluble homopolymer of a non-aromatic monoolefin having between three and twenty carbon atoms, said polymer having a number average molecular weight of about 750 to about 10,000 and present in an amount so as to allow the lubricating oil composition to be multigraded according to SAE standard, in the multigrade range between SAE 75W and SAE 250.

25. A composition as claimed in claim 24 wherein the homopolymer is polyisobutene having a number average molecular weight of about 900 to about 5000.

26. A concentrate comprising (B) an extreme pressure agent and (C) at least one oil-soluble homopolymer of non-aromatic monoolefins having at least three carbon atoms, said polymer having a number average molecular weight of about 750 to about 10,000, the amounts of (B) and (C) incorporated in said concentrate being such that when about 75 to about 25 parts by weight of said concentrate is blended with about 25 to about 75 parts by weight of at least one base oil of viscosity of about 40 to about 2,000 SUS at 100°F., the resulting blend is a lubricating oil composition which incorporates about five to about 70 weight percent of (C) and which is multi-graded according to SAE standards within the multigrade range of SAE 75W to SAE 250 exhibiting extreme pressure

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1043322

properties, said base oil being selected from the group consisting of natural oil, synthetic oils and mixtures of about 5 to about 95 weight percent of at least one natural oil and about 95 to about 5 weight percent of at least one synthetic oil.

27. The concentrate claimed in claim 26 wherein there is also present about 0.5 to about 5 percent of a pour point depressant.

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